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Stabilization/solidification of hot dip galvanizing ash using different binders

S. Vinter[a], M.T. Montanes[b], V. Bednarik[a,*], P. Hrivnova[a]

[a] Department of Environment Protection Engineering, Tomas Bata University in Zlin, Faculty of Technology, Vavreckova 275, 760 01, Zlin, Czech Republic
[b] Ingeniería Electroquímica y Corrosión. Departamento de Ingeniería Química y Nuclear. Universitat Politécnica de Valencia (Polytechnic University of Valencia), Camino de Vera s/n, 46022, Valencia, Spain

HIGHLIGHTS

- A stabilization/solidification of zinc-containing hazardous waste is studied.
- Portland cement and coal fly ashes are used as binders.
- Statistical regression analysis is used for finding the best mixture composition.

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ABSTRACT

This study focuses on solidification of hot dip-galvanizing ash with a high content of zinc and soluble substances. The main purpose of this paper is to immobilize these pollutants into a matrix and allow a safer way for landfill disposal of that waste. Three different binders (Portland cement, fly ash and coal fluidized-bed combustion ash) were used for the waste solidification. Effectiveness of the process was evaluated using leaching test according to EN 12457-4 and by using the variance analysis and the categorical multifactorial test. In the leaching test, four parameters were observed: pH, zinc concentration in leachate, and concentration of chlorides and dissolved substances in leachate. The acquired data was then processed using statistical software to find an optimal solidifying ratio of the addition of binder, water, and waste to the mixture, with the aim to fulfil the requirement for landfill disposal set by the Council Decision 2003/33/EC. The influence on the main observed parameters (relative amount of water and a binder) on the effectiveness of the used method and their influence of measured parameters was also studied.

1. Introduction

Metal industries, such as galvanizing, casting, smelting, and several others produce a large amount of waste containing high content of zinc. It is estimated that about 55% of zinc resources are used for galvanization. This technique is a multilevel process. As the first step, steel pieces are chemically degreased in a bath containing bacteria and surfactants to easily remove oil and fat, after that, the rust on surfaces is removed, and then they are put into a bath of molten zinc at 450 °C. By this process, the pieces gain a thin layer of zinc (150 μm) on their surfaces. This procedure produces two types of waste. The first type of waste is a sludge, which is generated after a pre-treatment of steel parts prior to dip into a bath of molten zinc. It contains about 65–75 wt.% of water and 25–35 wt.% of solids, mainly iron a zinc compounds. The second type of waste is hot-dip galvanizing ash collected from air filters above the bath with a molten zinc. This waste contains considerable amounts of zinc, its compounds and ammonium chloride [1–4].

The US Environmental Protection Agency (US-EPA) lists zinc as a priority pollutant because it is harmful for the environment and only 0.3 mg/kg/day is a reference dose for chronic oral exposure in humans [5]. Thus it is necessary to prevent the zinc ions from leaching to the environment [6]. One possibility is using the stabilization/solidification technique, which immobilize toxic metal into a matrix made from a suitable binder and is often used for the treatment of industrial hazardous waste [7].

The most common method of stabilization/solidification (S/S) uses Portland cement as the binder. Moon et al. [6] and also Trezza [8] reported that zinc reacts with cement clinker during

* Corresponding author.
E-mail addresses: tmontane@iqn.upv.es (M.T. Montanes), bednarik@ft.utb.cz (V. Bednarik).

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hydration. Calcium hydroxide $Ca(OH)_2$ is the main phase that fix zinc in cement matrices and the zinc solubility is controlled by calcium zincate ($CaZn_2(OH)_6{\cdot}2H_2O$). Zinc is also associated with increased formation of ettringite, which causes expansion and cracking of cement under some circumstances [9]. However, other studies [6,8,10] indicated that the ettringite, which is formed during the cement hydration process, affecting metal immobilization by replacing of Ca^{2+} ions with metal cations, e.g. Zn^{2+}. Formation of a low-soluble calcium zincate was also considered as the cause of zinc immobilization in calcium systems [11] and interference with the cement hydration resulting in decrease of compressive strength and retardation of hardening process [8]. Similar mechanisms was observed while fly ash was used as the binder [12,13]. Many authors have also reported that the pH value had a significant effect on fixation of heavy metals in the solidified waste [14–16]. The zinc in aqueous systems prevails in the form of Zn^{2+} cations in pH <8.5, in the range of pH values between 8.5 and 11.5 forms low soluble zinc hydroxide, and in the pH >11.5 it is dissolved as zincate anions and can be easily leached out from the cement-based solidified waste [17]. Thus, the waste with a high zinc content could be intractable by this way.

The goal of this study is optimizing the stabilization/solidification process of hot-dip galvanizing ash using three different binders to find the optimal ratio between the addition of a chosen binder, ash and water, considering the environmental safety of the solidified waste landfill disposal and minimization of the operational and landfilling costs. Very few studies considered the effect of variability in water and binder proportions [18]. The approach presented in this paper uses different water and binder contents and the statistical regression analysis method of finding the best mixture composition for the S/S treatment of the waste.

2. Experimental

2.1. Waste

The sample of waste was collected from the factory Galvanizadora Valenciana, S.A located in Spain near Valencia, where galvanized steel pieces are produced. The waste is a dust collected by air filters at the treatment of hot gasses generated above the surface of molten zinc in the bath at about 450 °C. It contained zinc in a form of metallic zinc, zincite (ZnO), and chlorides which are in the form of simonkolleite $Zn_5(OH)_8Cl_2{\cdot}H_2O$ and $ZnCl_2$.

2.2. Binders

The waste with high content of zinc was treated using three types of binders and their combination. The chemical composition of selected binders is summarized in Table 1. Ordinary Portland Cement (OPC) II/B – S was obtained from the company CEMMAC Inc. (Hornie Srnie, Slovakia). The second binder was fly ash (FA) and it was obtained from heating plant in the town of Otrokovice (Czech Republic) and the last binder was a by-product of fluidized-bed combustion of coal (FBC) and it was collected in heating plant in the town of Zlin (Czech Republic).

Table 1
Chemical composition of binders (wt.%) by energy-dispersive x-ray fluorescence.

	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	SO_3
OPC[1]	9.88	32.5	6.33	45.5	0.02	0.87	4.96
FA[2]	33.4	56.1	3.14	2.04	1.01	3.98	0.36
FBC[3]	23.3	29.4	3.43	28.7	0.39	3.15	11.6

1–ordinary Portland cement, 2–fly ash, 3–fluidized-bed combustion ash.

2.3. Stabilizing and solidifying of hot-dip galvanizing ash

The solidifying mixture was prepared from the waste, different type of binder and water. The binder and the waste were blended for 5 min then water was added and the mixture was blended for about 10 min until it had a pasty structure. After that, the mixture was poured into plastic forms with the length of 92 mm, width 43 mm, and height 50 mm. The forms were covered with plastic covers and the samples were cured at ambient conditions for 28 days. After that, the solidified samples were evaluated after standard curing age of 28 days according to EN 197-1 [19]. After this time of curing the samples were dried and according to EN 12457-4 the evaluating parameters in the leachate were determined [20].

The experimental work was designed considering the following parameters:

- The relative amount of hot-dip galvanizing ash in the solid components of the mixture, ranged from 45 to 90 wt.%, and it was balanced with cement or different binder.
- The relative amount of water added to the mixture, ranging from 10 to 40 wt.%
- Ordinary Portland Cement with 65–79% of clinker, 21–35% of slag and ratio $SiO_2/Al_2O_3 = 3.29$.
- Fly ash with 56% SiO_2 and ratio $SiO_2/Al_2O_3 = 1.68$.
- Fluid product with a ratio $SiO_2/Al_2O_3 = 1.26$.

The nomenclature for the mixtures was following B-X-Z, where B was the type of a binder used, X was the relative amount of water added to the mixture and Z was the relative amount of binder added in the solid components of the mixture. B was different for every binder added to the mixture, so that BI refers to cement, BII refers to fly ash, BIII refers to product of fluidized-bed combustion of coal.

For example, the ratio BI-19-10 was prepared from the addition of 19 wt.% relative amount of water and balanced with solid components from which, the cement addition was 10 wt.% and the waste addition was 90 wt.%. That means this mixture was made from 8.1 g of cement, 72.9 g of waste, and 19 mL of water.

2.4. Acid digestion

For the determination of total zinc concentration in dry matter of the ash, mineralization method in sulphuric acid was used. The process was performed in the following way: 5 g of sample was weighed and put into a beaker with 60 ml of 0.5 M H_2SO_4. The mixture was stirred for 15 min, then the solution was poured into 250 ml flask, completed with distilled water and homogenized. After that, the liquid phase was filtered through a 0.45-μm filter and subjected to the chemical analysis.

2.5. Leaching tests

Leaching tests using distilled water to evaluate the zinc concentration, retention capacity, the concentration of chlorides, and the concentration of dissolved substances were performed in triplicate. Solidified samples were evaluated after 28 days of curing. Leaching tests were performed using distilled water at the solid/liquid ratio 1/10 by weight. The leaching procedure consisted of the following: 50 g of pulverized sample (untreated or solidified waste) of particle size less than 10 mm were mixed with 500 ml of distilled water during 24 h under permanent shaking at room temperature on a vibrating shaker at the shaking frequency 150 rpm. Afterwards, the liquid phase was filtered through a 0.45-μm filter, and then was analysed by atomic absorption spectrophotometry.

The European regulation 2003/33/EC establishes the criteria for the acceptance of waste at landfills, which are based on EN 12457-4 leachability test [20,21]. Table 2 shows the leaching limit values